

Introduction

It has historically been difficult to analyze aluminum by ion chromatography because it is usually present as a trivalent cation (Al^{+3}) and strongly bound to the cation exchange resins used for cation separations. The use of the divalent phenylenediamine mobile phase allows the separation of the trivalent aluminum on a cation exchange column with conductivity detection. UV detection can also be used for the detection of trivalent aluminum. The column effluent is mixed with a post column reagent to form a metal complex that is visible in the 310nm range.

The Alltech Cation/R column is used for both methods presented here. This column is a poly (styrene-divinyl benzene) based resin with sulfonated functional groups. Fortier and Fritz developed the separation of aluminum using p-phenylenediamine, as the driving ion on the Cation/R column¹. The p-phenylenediamine mobile phase is adjusted to a pH of 3 with perchloric acid to provide the diprotonated driving ion. Under these conditions, aluminum elutes later than most divalent metal ions and well before most other trivalent metal ions.

Post column reaction of Tiron (4,5 dihydroxy-m-benzene disulfonic acid disodium salt monohydrate) with the column effluent provides an aluminum-Tiron complex that is detected with UV at 310nm. The Cation/R column is used with an mobile phase containing sulfuric acid and ammonium sulfate to separate aluminum from other trivalent metal ions.

Results and Discussion

The analysis of aluminum using phenylenediamine and conductivity detection is shown in **Figure 1**. The mobile phase is prepared by adjusting an aqueous solution of 16.5mM p-phenylenediamine to a pH of 3.0 with perchloric acid. This method allows the detection of aluminum in the presence of other metals. The divalent metals such as magnesium, manganese, zinc, cobalt, calcium and strontium elute in the void volume of the column under these conditions. If the concentration of the phenylenediamine mobile phase is decreased, these divalent metals will be retained and separated on the Cation/R column. Trivalent metals such as lutetium and thulium elute after aluminum using these conditions. By increasing the concentration of the mobile phase these metals will elute within a reasonable time. Detection limits for aluminum using this method are in at the low ppm level.

Aluminum analyzed using post column reaction and UV detection is shown in **Figure 2**. The mobile phase for this separation is an aqueous solution of 5mM sulfuric acid and 100mM ammonium sulfate. A colorimetric reagent is added to the column effluent to react with the eluted aluminum ions to form a colored complex. The Alltech RDR-1 pneumatic delivery system is used at room temperature to add the post column reagent to the column effluent without flow fluctuations. A peristaltic or piston pump should not be used since delivery systems that produced flow fluctuations will produce noise in the baseline. The post column reagent and the column effluent are mixed in a 5 foot reaction coil. Tiron is used as the color forming agent for aluminum. The post column reagent is prepared by adjusting the pH of a 3M ammonium acetate solution to 6.2 with 0.1M sodium hydroxide. Tiron is added to provide a 0.3mM concentration in this solution. This method also allows for the determination of aluminum in the presence of other metal ions. The 310nm wavelength is selective for the aluminum-Tiron complex. Detection of low ppb concentrations of aluminum are possible with this method. The ferric-Tiron complex is also detected at this wavelength. See **Figure 3** for this separation.

Conclusion

Trivalent aluminum can be separated by cation exchange and detected by conductivity or UV. Conductivity detection with a phenylenediamine mobile phase provides aluminum detection in the ppm range. Low ppb concentrations can be detected by UV after forming the aluminum-Tiron complex with post column reaction. Both of these separation methods provide the determination of aluminum without interferences from other di and trivalent metal ions.

¹ Fortier, N.E., Fritz, J. S. *Talanta*, 32 (1985) 1047-1050.

Aluminum Analysis with Conductivity Detection



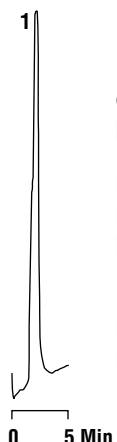
CHROM
6162

1. Al³⁺

Column: Cation/R, 100 x 3.2mm
Mobile Phase: 16.5mM p-Phenylenediamine, pH 3.0 with Perchloric Acid
Flowrate: 1.0mL/min
Detector: Conductivity

Figure 1

Aluminum Analysis with Post Column Reaction and UV Detection



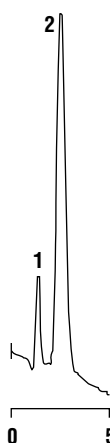
CHROM
6161

1. Al³⁺

Column: Cation/R, 100 x 3.2mm
Mobile Phase: 5mM Sulfuric Acid, 100mM Ammonium Sulfate
Flowrate: 1.0mL/min
Post Column Reagent: 0.3mM Tiron in 3M Ammonium Acetate pH 6.2 with Sodium Hydroxide
Reagent Flowrate: 0.6mL/min
Detector: UV at 310nm

Figure 2

Aluminum and Fe Analysis



CHROM
6160

1. Fe³⁺
2. Al³⁺

Column: Cation/R, 100 x 3.2mm
Mobile Phase: 5mM Sulfuric Acid, 100mM Ammonium Sulfate
Flowrate: 1.0mL/min
Post Column Reagent: 0.3mM Tiron in 3M Ammonium Acetate, pH 6.2 with Sodium Hydroxide
Reagent Flowrate: 0.6mL/min
Detector: UV at 310nm

Figure 3

Description

Part No.

STAINLESS STEEL COLUMNS	
Cation/R, 100 x 3.2mm	269004
Cation/R, 50 x 4.6mm	269024

Description

Part No.

METAL-FREE COLUMNS	
Cation/R, 50 x 4.6mm	269025